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Thermal & Electrical

Conductivities of the Alkali Metals

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THERMAL AND ELECTRICAL CONDUCTIVITIES OF THE ALKALI METALS

BY

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B. S. Illinois Wesleyan University, 1906A. M. University of Illinois, 1909

THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOHN WESLEY HORNBECK

THERMAL AND ELECTRICAL CONDUCTIVITIES ENTITLED

OF THE ALKALI METALS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS

M. F. Coarman Jakob Kintz In Charge of Major Work Head of Department

Final Examination

Committee



CONTENTS

	Page
Introduction	1
Theory of the Method	7
Apparatus	11
Experimental Details	17
Data Tables	23
Curves	30
Discussion of Results	30
Summary	32



One of the first successes of the modern electron theory consisted in its very simple explanation of the constant ratio of the thermal and electrical conductivities for the metallic elements. However, a closer study of the conduction of heat and electricity through metals, of their thermo-electric and magnetic properties, showed that the simple theory, which considered the electrons to move freely through the metal, was unable to explain the manifold and complicated phenomena in a satisfactory way.

It was first assumed, in the theories of Riecke, Drude, J.J. Thomson and H. A. Lorentz, that the electrons are free and share the heat motion of the atoms; but this assumption leads to a number of contradictions. When one determines N, the number of free electrons per cubic centimeter, by the method of the conductivities for heat and electricity for the different metals, values are found which differ greatly from those derived from the Peltier effect. Moreover, the experiments of Rubens and Hagen show that the electrical conductivity of metals for alternating currents of very high frequency remains practically the same as for steady forces, and the values of N which follow from these data are impossible in view of the Imcwn values of the specific heat. Furthermore, Lees measured the thermal and electrical conductivities of a number of metals down to the tomperature of liquid air and found an increasing deviation from the law

$$\frac{\lambda}{\nabla} = \frac{4}{3} \quad \frac{\alpha^2}{e^2} \quad T$$

Also it has been found recently that at the very lowest temperatures

^{(1),(2)} J. J. Thomson, Corpuscular Theory of Matter, pp 76, 84.

⁽³⁾ C. H. Lees, Phil. Tran., Royal Soc., Vol. 208, p. 381, 1908.

⁽⁴⁾ O. W. Richardson, Trans. Am. Chem. Soc., Vol. XXI, 1912.



the electrical resistance disappears suddenly. These facts can not be explained by the present theories, even when it is assumed as (4)
Richardson has done, that the distribution of the velocities of the electrons is that which corresponds to Maxwell's expression.

The strongest evidence against this conception of the electric current consists in the fact, shown by Nernst, that the specific heat of metals approaches zero as the temperature approaches the absolute zero. If the current were due to the motion of free electrons which are in temperature equilibrium with the metal, then the specific heat would be due mainly to the free electrons and would therefore, as in a gas, change very little with decreasing temperature. The question arises as to whether the electrons carrying the current take part in the specific heat.

Several modifications of the original theory have been proposed, but none of them gives an adequate quantitative explanation of all the phenomena. The various theories agree only in the fundamental assumption that the current is carried by electrons. This is in harmony with the general facts that the good conductors are metals, positive elements, ready to part with a negative electron; that the metals when struck by ultra-violet light or Roentgen rays, or when heated to a certain temperature, emit electrons; and that the current in the metals shows the Hall effect.

The decrease of the specific heat with decreasing temperature is at least qualitatively accounted for by Planck's theory of radiation. It is possible that the electrons have at low temperature no part in the specific heat of the metals, so that the specific heat is entirely due to the motion of the atoms or to their elementary oscillators. According to this conception there are no free electrons at all, at least at low temperatures, and the electrons escape only when they



have acquired a sufficient amount of kinetic energy to overcome the attraction of the positive "rest-atom." Then there should be a definite relation between the energy of the electron and the energy of the atom.

We shall assume that the electrons part with the atom when their kinetic energy is proportional to the energy E of the atom. Moreover, for the energy of the atom, or the oscillator in the atom, we shall assume the expression given by Planck

$$E = \frac{hn}{hn}$$

$$e^{kT} - 1$$

or, according to the mcdified theory,

$$E = \frac{hn}{hn} + \frac{hn}{2} \cdot \frac{kT}{2}$$

Then the kinetic energy of the electron is given by

$$E_1 = \frac{1}{2} \text{mv}^2 = F \frac{\text{hn}}{\text{hn}},$$

$$e^{kT} - 1$$

where f is some constant, and from this equation we know v as a function of T. The constant term $\frac{hn}{2}$ has no effect in the present application of the Planck theory. If \underline{l} is the mean free path and \underline{t} the time during which the electron moves from one atom to the other, then

$$v = \frac{1}{t}$$

The force acting on the electron in the field $\mathcal E$ is $\mathcal E$ e, and the acceleration

$$a = \frac{\mathcal{E}_{e}}{m}$$
.

The mean time during which this force acts is $\frac{t}{2}$ seconds and hence the field superposes a velocity

⁽⁵⁾ Planck: Acht Vorlesungen über Theoretische Physik.



$$u = \frac{at}{2} = \frac{\mathcal{E}_{el}}{2mv} .$$

The number of electrons passing through unit cross-section per unit time is

$$Nu = \frac{N \mathcal{E}_{\theta}1}{2mv}$$

and the current density

$$i = Nue = \frac{\mathcal{E}_0^2 Nly}{2my^2} = \sigma \mathcal{E}.$$

Whence

$$\sigma = \frac{e^{2} \text{Nlv}}{2 \text{mv}^{2}} = \frac{\text{Nlve}^{2}}{4 \text{E}_{1}} = \frac{\text{Nlve}^{2}}{4 f \frac{\text{hn}}{\text{nn}}}$$

$$e^{kT} - 1$$
(1)

For the quantity of heat energy passing through unit area per unit time, we have

$$H = \frac{1}{3} \text{ Nvl } \frac{\partial E_1}{\partial x} = \frac{1}{3} \text{ Nvl } \frac{dE_1}{dT} \frac{dT}{dx} = \lambda \frac{dT}{dx} .$$

And

$$\lambda = \frac{1}{3} \text{ Nvl } \frac{dE_1}{dT} - \dots$$
 (2)

Hence

$$\frac{\lambda}{\sigma} = \frac{4}{3e^2} \frac{dE_1}{dT} \cdot E_1 - \dots$$
 (3)

Substituting in (3) the values of
$$E_1$$
 and $\frac{dE_1}{dT}$, we have
$$\frac{\lambda}{\sigma T} = \frac{4}{3} \frac{\mathcal{F}^2 h^3 n^3}{e^2 k} \frac{1}{T^3} \frac{e^{kT}}{hn} - \dots - \frac{1}{\sigma}$$
 (4)

If hn is small, we can expand the expenential functions and equa tion (4) for the higher temperatures assumes the form

$$\frac{\lambda}{6T} = \frac{4}{3} \quad F^2 \frac{k^2}{e^2} \left(1 - \frac{hn}{2kT}\right) - - - - -$$
 (5)

As T increases, according to equation (5), the values of $\frac{\lambda}{\sigma_{T}}$ should approach a constant value and this agrees with the facts.

Moreover, when the values of $\frac{\lambda}{\sigma T}$ are plotted against T in equation (4),



the curve is found to be of the same form as the experimental curves which Lees obtained for the pure metals at low temperatures. Thus we have a formula which explains the behavior of $\frac{\lambda}{6}$ and which also leads approximately to the right expression for the variation of the specific heat with the temperature. It agrees with Einstein's formula for specific heat.

It is not claimed that this theory is complete. For example it does not account for the increasing heat conductivity at low temperatures. But it is suggested as a possible step in the right direction because it removes two of the greatest difficulties of the electron theory without introducing new contradictions.

It was the purpose of the present investigation to attempt to bring further evidence in favor of one of the different theories. The alkali metals were thought to be particularly suited to this purpose because they have properties quite different from those of the other metals. The alkali metals emit positive particles in a vacuum at ordinary temperatures and assume a negative potential, while the ordinary metals emit positive particles only at higher temperatures.

Alkali metals have a higher temperature coefficient of resistance than the other metals. The atomic heat and atomic volume are greater and the index of refraction smaller than for the ordinary metals. In their photo-electric properties they differ considerably from the other elements. All these properties indicate that the alkali metals are rich in electrons and that even the positive "rest-atoms" have conciderable robility.

So far as known, the heat conductivity of the alkali metals has hitherto not been measured. This is a constant of sufficient importance to make its determination worth while. Northrup has determined

⁽⁶⁾ E. F. Northrup., Trans. Am. Electro-Chem. Soc. Vol. XX,1911,p185.



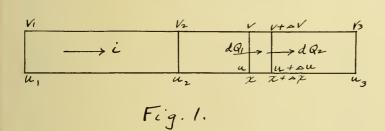
and claims an accuracy of one-half of one per-cent. His results, however, do not agree well with those of former observers and it was therefore considered important to check his work by a method entirely different.



II. THICKY OF THE STILL

The original contracted, which was a resolution of the contract of the contracting while the temperatures of the ends of the rod and of the surranging justice or held constant.

Referring to Fig. , lot u and v represent the temperature and potential of any cross-section of the rod; and lot



Thomson effect is negligible

and that λ and σ , for the small temperature interval considered, are consistent. Then the current flowing through the red is given by

$$i = \left(-\frac{dv}{dx}\right) \sigma a$$

And the number of calcries of heat developed in the elementary volume por whit time is

$$d Q = \frac{i^2}{6} \cdot \frac{dx}{a} \cdot \frac{1}{J}$$

(7) F. Achlrausch, Gött. Machr. S. 83, (1874).

Pogg. Ann., 156, S. 616, (1875).

Ann. der Phys., (4) I., 145, (1900).

(8) Jacger und Diesselhorst, Wiss. Abh. d. P. Phys. Tech. Reich., 3, 260, (1800).
Sitz. Ber. der Berlin Ak. d.w., 30, 719, (1800).



when J represents Joble's quivelint.

$$1 \cdot Q = \left(\frac{\mathrm{d} v}{\mathrm{d} x}\right)^{\nu} \mathcal{G} + \frac{1}{J} .$$

"... quantity or next flowing into the clomentary volume per unit

$$d \circ_1 = (-\frac{au}{dx}) \lambda a$$

13 the quantity flowing out is, likewise, equal to

$$1 Q_2 = -\frac{du}{dx} \lambda a - \frac{d^2u}{dx^2} \lambda a dx.$$

For the stationary state

$$dC + dC_1 - dC_2 = 0 - - - - - (1)$$

out tituting in this equation, we have

Now the isothermal surfaces are also equipotential surfaces, if we assure that the temperature is constant for all points of the same cross-section, and the temperature depends upon the potential only.

Then

$$\frac{du}{dx} = \frac{du}{dv} \frac{dv}{dx}$$

1.nd

$$\frac{d^2 u}{dx^2} = \frac{d^2 u}{dy^2} \left(\frac{dy}{dx}\right)^2 + \frac{du}{dy} \frac{d^2 y}{dx^2}.$$

Put

$$\frac{d^2v}{dx^2} = 0.$$

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dy^2} \left(\frac{dy}{dx}\right)^2.$$

Cultituting this value in equation (2), we have

$$\left(\frac{\mathrm{d} \mathbf{v}}{\mathrm{d} \mathbf{x}}\right)^{2} \stackrel{\mathbf{C}}{=} + \lambda \frac{\mathrm{d}^{2} \mathbf{v}}{\mathrm{d} \mathbf{v}^{2}} \left(\frac{\mathrm{d} \mathbf{v}}{\mathrm{d} \mathbf{x}}\right)^{2} = \mathbf{c}.$$

Or

$$\frac{d^2 u}{dv^2} = -\frac{S}{J\lambda} \tag{3}$$



Tring we be their equation, we called

$$\frac{\lambda J}{62} = -\frac{V^2}{2} + \Delta V + B - - - - - \qquad (')$$

The interaction constant, and P, are really well to be imposing the condition.

$$u_1 = u_3 = u^*$$

and the equation can be reduced to the form

$$\frac{\lambda}{69} = \frac{1}{8} \cdot \frac{1}{J} \cdot \frac{(v_1 - v_3)^2}{u_2 - u_1} - - - - -$$
 (5)

where up is the engineture of the riddle of the rod, and v' is the company ture of either of the two sections equally distant from the middle.

eral surface of the rod. This condition, however, cannot be realized experimentally and so it is necessary to apply a correction.

Let us change (5) slightly by expressing λ in watt-seconds, instead of calories, and put

$$V = \frac{1}{2}(v_1 - v_3)$$

$$U = u_2 - u' = u_2 - \frac{1}{2}(u_1 + u_3).$$

Then we have

$$\frac{\lambda}{\sigma} = \frac{V^2}{2U} - \dots$$
 (ϵ)

In this equation, then, U stands for the value of the temperature difference, supposing that the surface of the rod were covered with a perfect heat insulator.

Now let 4 represent the observed value of the temperature interval $u_2 - \frac{1}{2}(u_1 + u_3)$; let u_0 represent the temperature of the surrounding jacket; and let $E = u_0 - u_2 + \frac{1}{6}\Delta$.

Then, as Jacger and Dicarelhorst have shown,

where ϵ is a correction factor depending or the conductivity of the



10

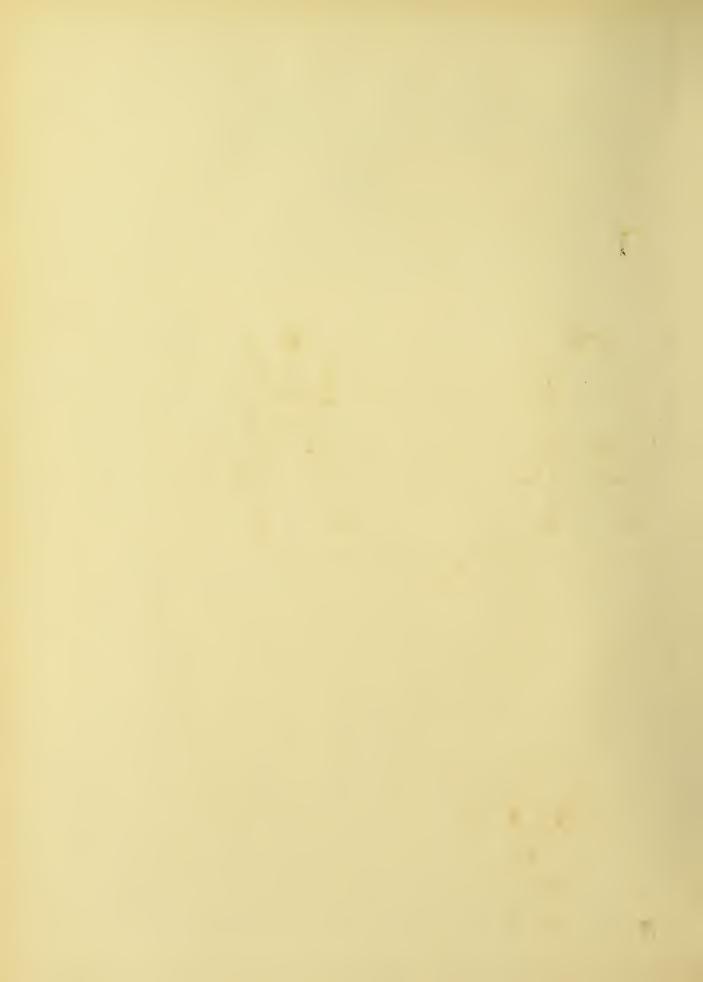
experimented upon; and its value out be determined by appring.

In the present work with the alkali metals, the values of λ/ε with the alkali metals, the values of λ/ε

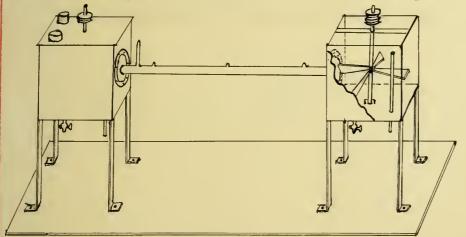
$$\mathcal{E} = \frac{\Delta}{N}$$

for the case where he heating current is used. The method of obtaining this served on factor will be made clark in a later chapter.

⁽⁹⁾ Wis. . Abh. der Thys. Tech. Reich., 3, 285, (1900).



End Eaths. The apparatus for controling temperatures was constructed in the Department shop. It was modeled after that of Jaegor and Diesselhorst, but certain modifications were necessary in order to protect the glass vacuum tubes which contained the alkali metals. The end baths were made of heavy tinned iron. They were cubical, 20 cm. on an edge, and stood 18 cm. high, leaving room for a Bunsen burner beneath them. Each was provided with a flat brass lid and a rotary stirrer, as shown in Fig. 2, which was driven by a small rotor at a speed of about 200 revolutions per minute. Fig. 3 indi-



cates the method
used to attach the
glass tubes to the
end baths. In a
way to be described
in detail later, the
metal to be studied
was poured into

Fig. 2.

glass tubes one or two centimeters in diameter and 30 cm. long. The ends of the tube were closed by copper discs, 2 mm. thick and 5 1/2 cm. in diameter, the axis of the tube being perpendicular to the plane of the discs. By means of suitable brass rings, each provided

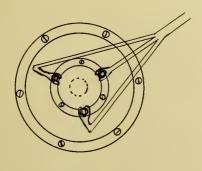


Fig. 3

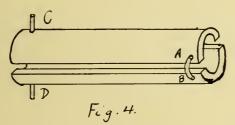
with six screws, the end-discs were attached to annular diaphragms which, in turn, were mounted against the end baths in a similar way; so that the alkali metal and the water were separated only by the thin discs of copper. The diameter of the openings



through the valls of the water baths was & cm. The soft-rubber disphragms served as a protection for the glass tubes against mechanical strains.

The heating-current terminals were introduced leneath the hoads of three of the screws symmetrically placed with respect to the center of the discs.

Brace Jacket. The temperature of the atmosphere of the tubes was controlled by pumping water from a reservoir through a cylindrical brase jacket by means of a small turbine. This jacket was made in two independent parts which were connected at A and B (Fig. 4), and



similarly on the opposite
side, by short rubber tubes,
thus making it necessary for
the water to flow the entire

length of both semi-cylinders before leaving the jacket. The wires of the thermo-couples were introduced between the two parts of the jacket and were insulated from the brass by thin strips of mica.

The temperature, u_o, of the jacket was measured by two Peckmann thermometers, mounted deep within vertical glass tubes through which the water flowed, so that no stem corrections were necessary. Moreover, these thermometers were placed so that their bulks were at axactly equal distances from the points C and D, respectively. The tubes leading from the jacket to the thermometers were made as short as possible, of course, and were packed each with the same number of layers of asbestos paper. Likewise, the glass tubes containing the thermometers were packed similarly so that, even though the two indicated temperatures which differed considerably, when working far from room-temperature, still the arithmetic mean of the two readings gave the true mean temperature of the water in the jacket.



The crace nurrounding the tube within the brase jacket we well of the picket with cotton wool and the cutside surface of the jacket we wranted with fourteen layers of heavy cotton flammel.

delyenor ter. The relamounter used was of the d'irecryal tyre and designed especially for work with thermo-couples. It was made 1, the leads and Morthrup Company of Philadelphia. It has a resistance of 230 ohms, a period of 4 sec., and a sensibility of 210 regolder for a scale distance of 1 mater. By means of an unusually good lens, however, the irage of a lamp filament was brought to a sharp focus on a scale 5 1/2 meters distant from the mirror. At 5 1/2 meters the sensibility was 5.6 x 10-10 amp. per mm deflection. The L.L.F. of the copper-constantan thermo-couples was about 40 micro-volts per degree, giving a deflection of (.2 mm per 1 degree. Thus a charge in temperature of one-thousandth of a degree could be detected. This was a higher sensibility than was needed in the work, since the temperature intervals measured were from two to three degrees, but it made the taking of readings a good deal more comfortable process, because, in balancing the potentiometer, the galvanometer deflections wors never reduced entirely to zero.

The logarithmic decrement of the galvanometer was not determined. Its value was such, however, that the coil would swing past the zero position no more than once in coming to rest. The spot of light on the scale remained very steady. No trouble at all was met due to vibrations.

Ammeters. With the exception of the potassium tube, where the value of the heating current sometimes exceeded 150 amperes, a new Siemens and Halske ammeter was used. It was standardized by means of a Wolf potention oter, Weston standard cell, and a standard 0.01-chm registance. The scale was found to be almost right. The correction



varied from +0.6% at 25 apperes, through zero at 65, to -0.3% at 1/c, and the curve was nearly a straight line.

For the date on potassium a Weston direct-reading ammeter (C - 200) was used. This was put in series with the reviameter (150-amp, shunt) and calibrated for the range over which it was used. Its constant for this range was +1.026. The 75-ampere shunt of the Cierces and Helshe instrument was also checked against the 150-ampere shunt.

When running the experiment the 75-argers shunt was used for all currents below this value and, as the scale was composed of 150 divisions on the Weston, practically all the deflections recorded represent readings of more than 100 scale divisions. The scale can certainly be read to 0.2 of a division and therefore the error in a single reading cannot be greater than 0.2%. However, when we consider the fact that the current was held constant by a controling resistance, that it required about two hours to make a run, and that the instrument was read at intervals of about five minutes during that time, the probable error, due to reading the scale, becomes insignificant.

Fotentiemeter.- An Otto Wolff potentiemeter of 15000-ohms resistance was used.

Resistance Boxes. The resistance boxes were also made by Otto Wolff.

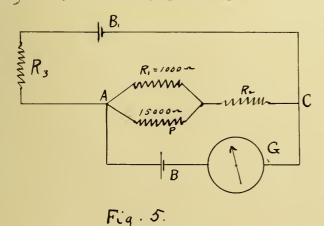
Standard Cell.- A Weston standard cell was used. It was certified by the Eureau of Standards at Washington.

Standard Thermometers.- All of the standard thermometers, except # 17451, were standardized at the German Reichsanstalt. Number 17451 (E.S. No. 6191) was certified by the Bureau of Standards. These thermometers were all graduated to tenth-degrees.



Battery. As a source of current the Department storage battery was available. This battery is composed of 80 cells, each cell having a discharge rate of 40 amperes and a capacity of 320 ampere - hours. Individual leads run from each cell to the main switch-hoard, making it an easy matter to group the cells into any desired combinations.

Arrangement of the Electrical Apparatus.— Since the E.V.F. of the copper-constant thermo-couples was approximately 40 microvolts per degree, it was convenient to have a current of exactly 4 micro-amperes through the potentiometer, so that the resistance for balance would indicate the approximate temperature directly. To accomplish this the potentiometer was connected, as shown in Fig. $\boldsymbol{5}$, in parallel with a resistance-box R_1 and this combination was in series with another resistance-box R_2 , a storage cell E_1 , and a third resistance-box R_3 . By suitably placing the switches, the galvanometer G and the



standard cell B₂ could be connected across AC for testing the potential difference. Making R₁ equal to 1000 ohms and assuming the drop in potential from A to C equal to the E.M.F. of the standard

cell, a simple calculation gave the value of R_2 for which the current through the potentiometer P was exactly 4 micro-amperes. Having made R_2 equal to this calculated value (14973.4), R_1 and R_2 were changed no more. The adjustment at the beginning of a run consisted merely in varying R_3 until the galvanometer deflection was reduced to zero.

The switches and keys of the rotenticmeter circuit which had to be operated continually while taking readings, were grouped together



ch one switch-board shown dir rammatically in C_1 and C_2 represent

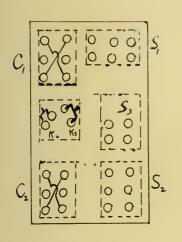


Fig. 6.

S₃ were two-way switches of the rocker type;

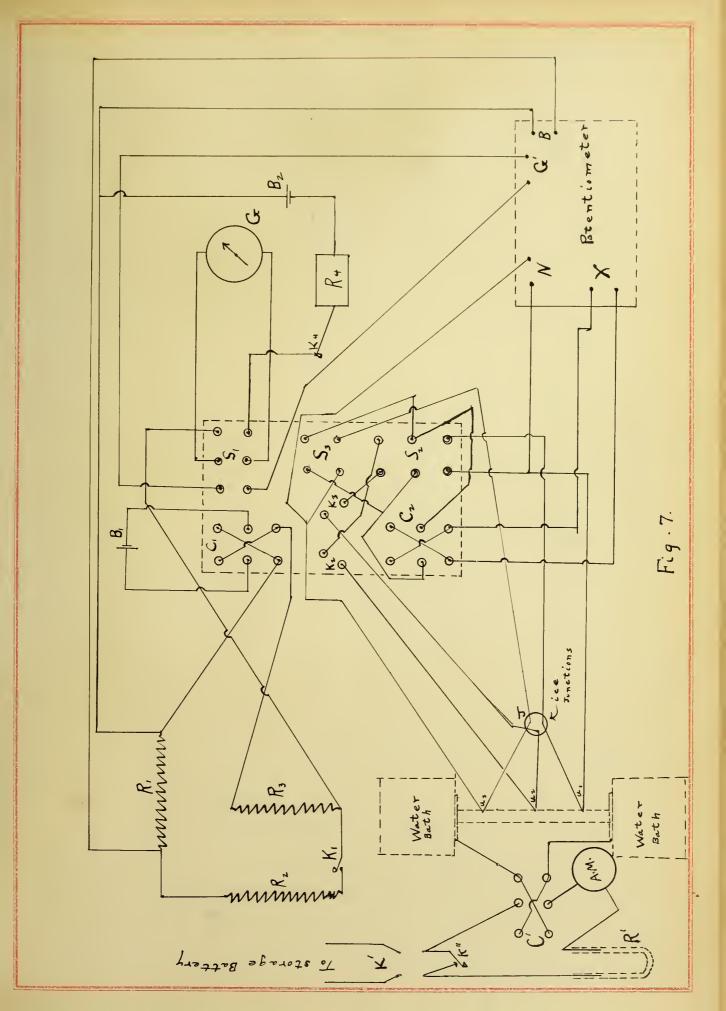
K₂ and K₃ were ordinary mercury keys. In the construction of this switch-teard, six tlocks of paraffire were used. They were mounted upon a glass plate, 30 by 40 cm., in the manner indicated by the dotted lines. The thirty-two mercury wells which were sunk in the paraffire, were all lined by small glass cups which served

as supports for the metal rockers. These rockers were all made of copper and only copper wires dipped into the mercury cups, all being wound from the same spool. In this way, contact potential differences were reduced to a minimum.

Fig. 7 shows a diagram of the exact connections of the electric circuits and the relative positions of the apparatus, with the exception of the galvanometer which was on a wall bench on the opposite side of the room, 5 1/2 meters away. The galvanometer scale was placed just above the potentiometer so that one observer, without changing his position, could balance the potentiometer, operate the switch-heard, regulate the resistance, and read the thermometers which gave the temperatures of the brane jacket and the water baths. Moreover, by moving only a couple of steps, the ammeter, A.M., commutator C', controling resistance R', and Key K", were all within easy reach. K" was a short-circuiting key to avoid arcing when the rocker of C' was thrown over. R4 was simply a protective resistance for the galvanometer and standard cell, and could be cut out of the circuit by a suitable plug.

The diagrams of Fig. 7 , are thought to be sufficiently clear to







be followed without further explanation.

IV EXPERIMENTAL DETAILS

Construction of Thermo-couples.— Since the alkali metals dissolve ordinary solder, it could not be used for the junctions which were placed in the tules. Moreover, it was not an easy matter to hard-colder the junctions without burning the minute copper wires. Several attempts to do this having failed, it was decided to try the use of mechanical contacts. The fine copper wire, 0.12 mm. in diareter, was would around the constantan wire (diam. 0.18 mm) for a distance of about 2 mm. The shape of these junctions was admirably adapted to the double purpose of measuring both the temperature and potential difference between two cross-sections. They were mounted in a tube of sodium-retassium alloy but the data was inconsistent and on removing the junctions from the tube and attempting to check their calibration, it was found that two of the three calibration curves had shifted by an amount equivalent to more than one-tenth of a degree

So it was considered necessary to solder the wires together. The method which finally succeeded was as follows: Nearly equal weights of copper and silver were melted together with a small blast flame.

A junction formed by two or three turns of the copper wire around the constantan, was moistened and covered with powdered borax. Then, at a time when the temperature of the silver-copper alloy was just above the melting point, the junction was dipped beneath the surface of the globule and quickly removed.

Junctions could be soldered in this way without any injury to the delicate wires. Such junctions, therefore, were used in the last three tubes experimented upon,— the three for which the data are given in this paper. The ice junctions were soldered with ordinary softsclder.



For the alloy tube and the potassium tube, copper wire 0.12 mm in diameter was used. However, it was found to be almost impossible to go through the long process of calibrating the thermo-couples, mounting them into the tube, filling the tube, and finally mounting the tube between the water baths, without breaking one of these frail wires at some point where it could not be soldered, — thus involving the loss of the thermo-couple and several days work. Consequently, somewhat larger copper wires were used in the sodium tube. In this case, the diameter of the wire was 0.16 mm. It can be shown, however, that the error due to the conductivity of this wire was negligible, for the conditions under which it was used. For all three of the tubes the constantan wire used had a diameter of 0.18 mm.

Flatinum-constantan thermo-couples were used in the lead rod because, at that time, it was thought platinum wire would be used in
the case of the alkali metals, since it could be sealed into the
glass, but the plan proved impracticable.

Calibration of the Thermo-couples. The thermo junctions and thermometer were mounted within a large Dewar flask which contained also a rotary stirrer. For the lower temperatures salt and ice were used to keep the temperature from rising, while for the higher temperatures steam was introduced slowly through a small tube near the wall of the flask at a point diametrically opposite the position of the thermo-junctions and thermometer. The temperature in this way could be held very steady by regulating the gas pressure of the three Punsen flames which heated the boiler. The rotary stirrer was run by a small motor.

For the first few calibration curves a cathetometer was used to read the thermometer scale. This, of course, was a most accurate method, but it involved the difficulty of holding the temperatures



constant for several minutes at a time, since the vernier had to be adjusted and read both before and after balancing the potentiameter for direct and reversed currents. Consequently, it was decided to try a direct-reading eye-piece attached to the stem of the thermoreter. By this method the data for a point on the calibration curve could be obtained so much more quickly that the loss in accuracy of the scale reading was almost compensated by the gain in time, and consequent smaller variation in the temperature. Readings were taken at intervals of about one or two-tenths of a degree over the particular range where the curves were to be used and, when the points were plotted, there was no doubt about the proper position of the line.

The curves obtained in this way were reliable to about three or four-thousandths of a degree, for the measurement of temperature differences; and, since this was as high a degree of accuracy as was required in the calibration, the use of the cathetometer was abandoned in favor of the quicker and less laborious procedure.

Fregaration of the Tubes. The kind of tube used to contain the alkali metals is shown in Fig. 8. The side tubes A, B, and C,



through which the thermo-junctions were introduced, were about 2 mm in diameter and 10 cm. apart. They were sealed on in such a way as to change the cross

section of the main tube as little as possible. The filling tube D was always placed at least 4 cm. from C. The diameters of the tubes are given in the data tables. The entire length in each case was about 30 cm.

Considerable difficulty was met in devising a method of sealing in the thermo-junctions so that a vacuum could be maintained at temperatures above the melting point of sealing wax. It was firally



accomplished in the following way: The two wires of the junctions, one of which in each case was contained in a minute, slightly funnelshaped glass tube for insulation purposes, were first sealed into the tube by means of "Quixo Caementium". This is a mineral cement, a commercial article, which was purchased from one of the local dealers. It dries very hard but it is somewhat porous and will hold a vacuum only a short time. Consequently, after the cementium had dried it was covered over with a layer of sealing wax. A kind called be Khotinsky cement was used because it has a higher melting point than the red, "Bank of England" wax. The caementium held the thermojunctions rigidly in their positions and when the tube was heated the air pressure could not force the soft wax into the tube.

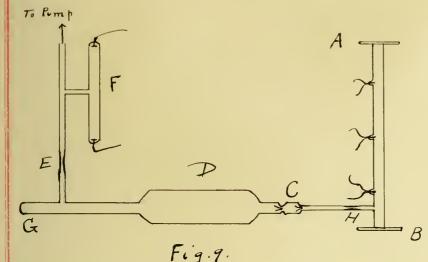
After grinding the ends of the tube they were fitted into circular grooves in the copper end-disks, about 1.5 mm deep. These joints were filled with litharge (PbO) mixed in boiled linseed oil, and baked for several hours at a temperature of about 100°C. When thoroughly dry and solid they were covered with a thick layer of the Khotinsky sealing wax. The reason for using litharge in place of caerentium, for sealing on the end discs, was the fact that it does not dissolve in water, - thus reducing the fire-risk in case of accident.

Before the end discs were sealed on, an accurate scale was introduced within the tube and the thermo-junctions bent into positions which spaced them exactly 10 cm. apart. They extended about 3 mm into the tube.

The sodium and potassium tubes were prepared as described above. Sealing wax alone, however, was used in the case of the sodiumpotassium alloy and for this reason no data could be taken with this tube for temperatures above 45°.



Filling the Tubes.- The method of filling the tubes is illustrated in Fig. q . The sodium or potassium was introduced into the



ing at G. The tube was then sealed at G and the Gaede pump started.

After melting the metal, it was kept het for an hour or more during the exhaustion, in order to

drive off all traces of the oil. When the crust finally appeared dry and black, and the discharge tube F showed only the presence of the alkali vapor, the system was sealed off at E. Then, holding AB in a horizontal position and keeping it hot with Bunsen flames, the tube D was tilted and the bright, pure metal poured through a system of small funnels at C which held back all of the dross. After sealing off at a stricture H, the experimental tube AB was ready to be mounted between the water baths.

Furity of the Metals.- The sodium and potassium were purchased from Eirer and Amend and, in a personal letter from the company, were claimed to be "very pure". I am indebted to Dr. G. McP. Smith of the Chemistry Department for the following test on the purity of these metals.

Sodium

- 1 Free from iron (KCNS test)
- 2 Free from calcium ((NH₄)₂ C₂O₄ test)
- 3 Free from Lagnesium (Na2HPO4 test)
- 4 Free from aluminum (no ppt. with NH40H- Na2HPO4test)
- 5 Free from potassium (H2PtCl6 test)



Spectroscopic test also negative, but conditions were not most favorable at time of test.

Fotassium

- 1 Free from iron
- 2 Free from calcium
- 3 Free from magnesium
- 4 Free from aluminum
- 5 Contains enough sodium to give a test with the spectroscope. Undoubtedly only a trace.

Method of Control of Tenperatures.- The apparatus for controling temperatures has been described in Chapter III. For the determinations above room temperature, the temperatures were adjusted and held constant by means of Bunsen flames, one under each end-bath and three beneath the large reservoir from which the water was pumped through the brass jacket. For the lower temperatures the turbine was discarded and cold water was run through the jacket by gravity pressure, the rate of flow being regulated by a small globe valve. In these determinations the temperatures of the end baths were watched constantly by a student helper and were maintained by the continuous addition of snow and salt.

Regulation of the Heating Current.— As already mentioned, the currents from the large storage battery were remarkably constant. The slight regulation necessary was accomplished with a mercury rheostat. The U-tube, which was made of glass tubing 2.6 cm. in diameter, stood 60 cm. high. Continuous adjustments could be made by varying the position of the copper-plated iron rods which dipped into the mercury



V DATA TABLES AND CURVES

In order to cut down the length of the paper the original data will be given only for a few typical runs. They will serve to illustrate the method of taking observations and to indicate the degree of consistency obtained at different temperatures. In the tables which follow these "specimen runs", merely the final results are recorded.

Meaning of Symbols.- In all the data tables the following notation is used:

r₁, r₃ = balance-resistance on potentiometer dial for thermocouples No. 1 and No. 3

r₂ = balance-resistance for thermo-couple No. 2 at middle of tube (or rod)

r' = balance-resistance when reading P.D.

u₁, u₂, u₃ = temperatures corresponding to resistances r₁, r₂, r₃

u = temperature of the brass jacket

 $u' = \frac{1}{2}(u_1 + u_3)$

 $t_m = \frac{1}{2}(u' + u_2) = temperature for which the values of <math>\frac{C}{\lambda}$, β , and λ are taken in plotting curves

V = one-half of the P.D. between the two points which were held at the same temperature

 $U = \Delta - \varepsilon N$

I = value of heating current in amperes

 $\Delta = u_0 - u^{\dagger}$

 $N = u_0 - u_2 + \frac{1}{6}\Delta$ $\varepsilon = \frac{\Delta}{N}$ when I = 0

The letters D and R in the tables represent direct and reversed currents through the potentiometer to eliminate contact potential differences

#2606 and #2607 refer to the two Beckmann thermometers which gave the temperature of the brass jacket



TABLE I

Constants for the Three Tubes

	Substance	Inside diameter	Area a	Effective length 1	
	Na-K Alloy	1.562 cm	1.916	20 cm	
	Fotassium	1.620	2.061	20 cm	
	Codium	1.234	1.196	20 cm	
=	$\frac{Ra}{1} = .0958h$	$= \frac{.0958 \times 2V}{I},$	for Sodiu	um-potassium alloy	
=	$\frac{0.103 \times 2V}{T}$	for Potassium	tube		
=	.0598 x 2V,	for Sodium tul	be		
	1	TABLE	II		

Correction Factor for Potassium Tube (Specimen Run)

	r ₁	r ₃	r ₂	#211	^u ₀ #212
D	187.8	187.7	197.2	2 20	1 76
R	186.8	186.8	196.2	2.20	1.36
D	187.5	187.8	197.0	2.18	1 75
R	186.6	186.9	196.2	2 • 1 0	1 • 35
D	187.5	187.8	197.0	2 10	1.30
R	1 86.7	186.9	196.3	2.19	
D	187.5	187.6	196.9	2.20	1.27
R	186.7	186.7	196.2	2.20	1 • 2 /
D	187.1	187.8	196.9	0 07	1.24
R	186.4	186.9	196.1	2.23	1 0 24

Left bath held at 18.4° ; right bath at 18.3° Mean temperature on #211 = $2.20 + 33.06 = 35.26^{\circ}$ Mean temperature on #212 = $1.30 + 32.91 = 34.21^{\circ}$ $u_0 = \frac{1}{2}(35.26 + 34.21) = 34.74^{\circ}$ C.

Mean $r_1 = 187.1$ ohms; $u_1 = 20.025^{\circ}$ Mean $r_2 = 187.3$ ohms; $u_3 = 19.965^{\circ}$ Mean $r_2 = 196.6$ ohms; $u_2 = 20.925^{\circ}$ $\Delta = 20.925 - 19.955 = 0.930^{\circ}$ $N = 34.74 - 20.925 + 0.155 = 13.97^{\circ}$ $\mathcal{E} = \frac{\Delta}{N} = \frac{0.930}{13.97} = .066$



TABLE III

Sodium-Fotassium Alloy at 5.7° (Specimen Run)

Main Current Direct Main Current Reversed

		11-100 4	11 0011		1000	414	W 111 0 W		110 101 11	
	r'	r ₁	r ₃	r ₂	u ₀ 2606	u _o 2607	r ₁	r ₃	r ₂	r'
D									6c.E	
R	3667	35.2	37.3	69.8	4.10	4.25	36.2	37.2	70.2	3661
D	7/5/	34.2	35.9	68.5	3.95	4.15	34.9	35.6	68.4	7 (().
H	3656	36.0	37.3	69.9	3.95	4.20	36.7	37.2	70.3	3664
D	7(5(34.2	35.9	68.6	3.94	4.20	34.8	35.5	68.4	7661
R	3656	36.0	37.4	70.0	3.90	4.15	36.8	37.2	70.4	3661
D	7(57	34.2	35 • 9	68.4	3.95	4.15	34.6	35.4	68.2	7667
R	3657	36.1	37.6	70.2	3.93	4.15	36.6	37.2	70.2	3663
D	7(50	34.1	35 • 7	68.3	3.98	4.17	34.6	35.4	68.1	7660
75	3658	75.0			7 07			77 0	70 1	3662

Left bath at -0.4°; right bath at 0° 6 volts, 6 sets in parallel I = 41.2 amp. Mean r_1 = 35.4 ohms; u_1 = 4.02° Mean reading on #2606 = 3.97 Mean r_2 = 36.6 ohms; u_3 = 4.04° Mean reading on #2607 = 4.20 Mean temp. on #2606 = 3.97 + 2.41 = 6.38°C. Mean temp. on #2607 = 4.20 + 2.76 = 6.96°C. Mean #2607 = 4.20 + 2.76 = 6.96°C. Mean #2607 = 4.20 + 2.76 = 6.96°C.

35.9 37.6 70.1 3.93 4.15 36.6 37.2 70.1

Sample Calculation

$$\Delta = 7.42 - 4.03 = 3.39 \qquad t_{m} = \frac{1}{2}(4.03 + 7.42) = 5.7^{\circ}$$

$$N = u_{0} - u_{2} + \frac{1}{6}\Delta = 6.67 - 7.42 + 0.57 = -0.18$$

$$U = \Delta - \epsilon N = 3.39 + 0.22 \times 0.18 = 3.43$$

$$\tilde{\chi} = \frac{2U}{V^{2}} = \frac{6.86}{(.00732)^{2}} = 128.1 \times 103$$

$$\tilde{\chi} = \frac{.0958}{41.2} \times \frac{.01464}{1.2} = 34040 \times 10^{-9} \text{ ohm}$$

$$\lambda = \frac{105}{4.19 \times 128.1 \times 3404} = .0547 \text{ cal.}$$



TABLE IV

Sodium at Room Temperature (Specimen Run)

	Mai	n Curre	nt Dire	ct		M	ain Cur	rent Re	versed	
	r ₁	r ₃	r ₂	r	#2606	#2607	r ₁	rz	r ₂	r'
D	187.6	190.9	215.0	7006	E /10	ヒルダ	187.6	188.9	217.1	3099
R	187.0	190.3	217.4	2096	5 •/+0	2.40	188.7	188.0	217.9	3099
D	188.3	190.5	218.0	7007	5 /1 Z	E E0	187.7	188.9	217.3	3098
R	187.3	189.6	217.2	グレガブ	7.47	5.96	189.5	187.9	218.2	7090
D	188.7	190.9	218.6	7.007	г /, «	5.56	188.2	189.0	217.6	3098
t .		190.3		1 (/ ~ 7)	2.40	2.50	189.3	188.2	218.4	3090
D	188.2	190.9	218.5	7007	г г7	r 61	188.1	188.9	217.4	700 Ø
R	187.4	190.2	217.5	2093	2.22	5.01	189.4	188.1	218.2	2090
Lef Mea Mea Mea Mea	it bath in r ₁ = in r ₃ = in r ₂ = in r =	12 set held at 188.2; 189.5; 217.8; 2096 oh N	$u_1 = 20$ $u_2 = 20$ $u_2 = 23$ $u_3 = 23$	righ 0.08° 0.12°	nt bath Temp. Temp. 2V = 2	n held on #26 on #26 uo = 2096 x	at 15.9 506 = 5.5 507 = 5.5 23.57° 4 x 10°	.46 + 18 .54 + 18	5.05 = 2 238 vol	23.59



TABLE V

Fotassium at 57.8° (Specimen Run)

Main Current Direct

Main Current Reversed

	r'	r ₁	r ₃	r ₂	#2 6 06	#2607	r ₁	1,3	r ₂	r'
D	7075	560.6	554.4	584.5	3.38	2.75	557.6	558.4	584.4	z 0 7 0
R	3075	559.0	556.2	582.6	3.37	2.76	556.0	559.8	583.0	3070
D	7071	556.0	553.5	582.8	3.38	2.76	555.7	557.9	583.6	7070
R	3071	557.8	555.2	581.0	3.42	2.77	553.8	559.6	582.0	3070
D	3078	557.4	554.9	584.1	3.43	2.78	557.7	557.6	584.3	3069
R	50/6	558.9	556.7	582.3	3.48	2.81	555.4	559.7	582.4	
D	707¢	553.6	555.9	584.3	3.42	2.83	558.1	555.3	584.3	7070
R	3078	555 • 3	560.6	582.5	3 • 35	2.81	555.6	557.1	582.4	3079
D	3074	554.4	555.9	584.4	3.27	2.73	557.8	555.2	584.0	707/
R	30/4	556.2	558.6	582.6	3.25	2.70	555.4	557.0	582.2	3074

Left bath at 51.0° Mean r_1 = 556.6; u_1 = 56.625° Temp. on #2606 = 3.38 + 54.98 = 58.36 Mean r_3 = 557.4; u_3 = 56.630° Temp. on #2607 = 2.77 + 55.13 = 57.90 Mean r_2 = 583.2; u_2 = 59.070° u_0 = 58.13° Mean r_1 = 3074 ohms; v_0 = 012296 volt v_0 = 2.443° v_0 = 57.8°

16 volts, δ sets in parallel I = 148.1 x 1.026 = 152.0 amp.

Right bath at 51.3°



TABLE VI

Values of Correction Factor ϵ

Substance	uo	u ₂	Δ	N	3
Lead Rod	21.7	16.47	೦.91 ೮	5.38	C.171
Na-I Alloy	21.19 24.46	15.40 19.86	1.35	6.C1 4.77	0.224
Lotassium	34.74	20.925	0.930	13.970	0.066
Sodium	41.60	18.66	1.38	23.37	0.059

TABLE VII

Corrlete Results for Lead (commercially pure)

Run No.	u _o	u ₂	t _m	2V 10 ⁻⁵ x	Δ	Z.	U	I amp.	10 ³ x
1	21.64	21.94	20.6	1253	2.671	0.14	2.647	51.0	134.6
2	21.65	23.60	21.7	1566	3.838	-1.32	4.062	63.3	132.5
3	21.71	23.28	21.3	1588	4.046	-0.90	4.199	64.3	133.2

Remark. For run No. 3, the lead rod was inside of a close-fitting glass tube.

TABLE VIII

Complete Results for Sodium-Potassium Alloy

(Masses taken proportional to the atomic weights)

Run No.	u_0	u ₂	t _m	2V 10 ⁻⁵ x	Δ	N	U	I amp.	10 ³ x	10-8 _x	λ cal.
1	-8.30	-8.28	-10.6	1511	4.56	+0.74	4.40	66.0	154.4	2193	.0705
2	-9.40	-6.37	- ర.9	1682	5.00	-2.20	5.48	72.9	155.2	2210	.0696
3	+6.67	7.42	5.8	1464	3.39	-0.18	3.43	41.2	128.1	3404	.0547
4	6.66	€.C7	6.2	1588	3.83	-0.77	4.00	44.6	127.0	3411	.0551
5	22.40	23.936	22.0	1684	3.931	-C.88	4.122	45.9	116.3	3515	.0584
6	22.54	24.075	22.1	1702	4.003	-0.86	4.190	46.2	115.9	3527	.0584
7	22.66	22.395	20.7	1500	3.453	+0.84	3.271	40.9	116.2	3513	.೧೯೮5
É	43.90	44.54	42.0	1550	3.17	-0.11	3.19	40.8	106.1	3640	.0610



TAPLE IX

Complete Results for Potassium

Rur. No.	u _c	112	t_{m}	2V 1C ⁻ 5x	Δ	T T	U	I amp.	σ/λ 10 ³ X	ohm 10-8 _X	λ cal.
1		5.790									
2	6.58	5.810	5.0	٤62	1.525	+1.02	1.454	137.5	156.5	644.2	0.237
3	21.16	21.670	20.7	1035	1.965	-C.18	1.978	151.6	147.7	703.5	0.030
4	21.22	21.590	20.6	1030	1.920	-0.05	1.523	151.2	145.1	701.5	C.^34
5	21.45	21.675	20.9	932	1.603	+0.04	1.600	137.6	147.4	697.C	0.232
6	58.13	59.070	57.ε	1230	2.443	-0.53	2.478	152.0	131.1	833.8	0.217
7	57.51	56.510	57.4	11.84	2.712	-0.01	2.326	147.3	132.4	835.3	0.216

TABLE X

Complete Results for Sedium

Run No.	uç	u ₂	t _m	2V 10 ⁻⁵ x	Δ	7.	U	anp.	σ/λ 10 ³ X	olim 10-8 _X	λ cal.
1	7.20	6.57	5.7	1152	2.68	+0.68	2.64	147.7	159.0	466.4	0.321
2	7.75	7.22	5.8	1176	2.82	+1.00	2.76	150.7	159.5	466.7	0.321
3	23.42	22.12	50.5	111C	2.385	+1.70	2.253	13C.E	140.2	500.3	C.317
4	23.57	03.01	21.5	1238	2.51	+1.05	2.05	146.3	148.8	506.0	0.317
5	43.30	43.24	40.1	1207	2.57	+0.31	2.55	128.3	139.7	502.6	0.304
6	44.57	43.34	41.7	1360	3.32	+2.14	3.19	145.5	138.1	559.0	0.309
7	62.30	62.84	61.3	1390	3.15	+0.01	3.15	137.2	130.4	605.8	0.302
క	63.11	60.83	61.4	1320	2.93	+0.77	2.58	130.7	130.1	604.0	0.200
00	55.01	89.43	క క.1	1309	2.67	+C.C3	2.67	112.0	124.8	663.4	C.288



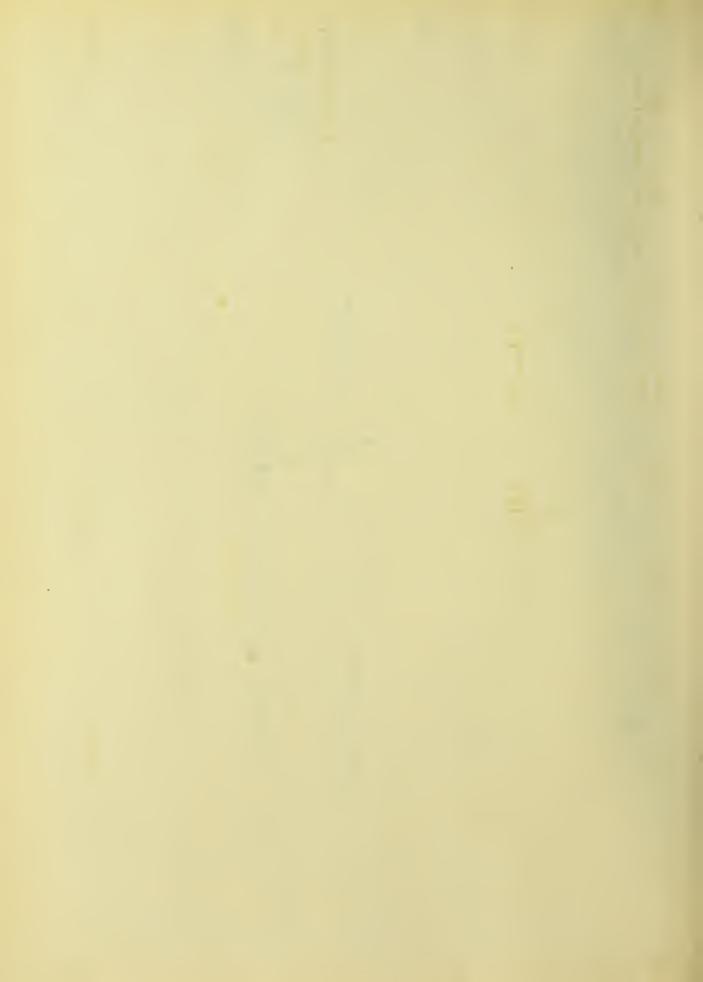
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correction factor & for the alk limitale, it was necessary to assume that for the stall state the temperature at corresponding points on the incide and outside surfaces of the glass tube were small; i.e., that the temperature gradient through the walls of the glass tube outlide be reglected in comparison with the drop in temperature through the sotten wool. One reason for making the mans with the local rol was to find out if this assumption would introduce an error large enough to be detected. Table VII answers the question. The fact that the value of the for run No. 3 falls between those for runs No. 1 and No. 2, proves that the effect of surrounding the rod with the glass was small or that other experimental errors. Lead was chosen for this experiment because of its low heat conductivity. The glass wall would have a still smaller effect in case of the sodium and potanticum.

Another reason for taking the data for lead was to have a means of comparing my results with those of Jacger and Piesselhorst. In this connection it should be noted that my average value of $\sqrt{\lambda}$ for lead at 01.5° is 133.4 x 10 3 while that of Jacger and Diesselhorst for pure lead, when reduced to 21.5° is 135.2 x 10 3 . This was considered a good check because the lead I used was only commercially pure. The presence of impurities always reduces the value of $\sqrt[6]{\lambda}$.

As to accuracy of results it should be pointed out that for each run stead; conditions were held for one to two hours and readings were taken continually during this time. Thus each value of u₁, u₂ and u₃, used in the calculations, depends upon sixteen to twenty readings on the potentiometer, while the values of V are computed from the sean of eight to ten readings. The current could be



the real of the potential difference did not made to be real to often.

Toronom, with the crew wealt of two or three interpretations.

The curve for \$\frac{\lambda}{\sigma}\$ bend here than were expected. It would be interpolating to know whether the, become straight lines at higher to persatures. Judging from the behavior of other notals, this should be expected. Lorsover, when \$\frac{\lambda}{\sigma}\$ is plotted against T, these curves alope devinward olightly with increasing temperature while least convex for most of the pure metals bend slightly upward at ordinary temperatures. Thus action and petassium, line nickel, are incregular in this respect. It should be noted that the heat conductivities of sodium and potassium decrease slightly with increasing temperature, while the heat conductivity of the alloy increases with the temperature. This is the law followed by rest motals and their alloys. The temperature coefficients of sodium and petassium are extremely high.

The mean values of the specific resistance of sodium and potassium at room temperature and the temperature coefficients are given below for convenience of comparison.

spec. res. of Na at 21.7°3 = 5072×10^{-9} ohm/cm³.

" " K " 20.7°C = 7010×10^{-9} ohm/cm³.

temp. coef. of Na = .00513, range 6° to 88°
" " K = .00552, " 5° to 58°

Northrup's Results

spec. res. of Na at 20°C = 4873×10^{-9} " " K " 20°C = 7116×10^{-9} temp. coef. of Na = .0053, range 20° to 80° " " K = .0058, " 20° to 50°

Matthiessen's Result

spec. res. of Na at $21.7^{\circ}C = 4464 \times 10^{-9}$

Bernini's Results

spec. res. of Na at 0.0° = 4739 x 10^{-9} = 6644 x 10^{-9}



Bernini's results, when reduced to room temperature, are found to be higher than mine and Northrup's, while Matthiessen's value is seen to be lower. It is thought that my results agree with Northrup's as closely as could be expected, considering the wide difference in method. Indeed his method is the more accurate one for electrical conductivity. Consequently, the results of this investigation may be said to confirm Northrup's work on the resistance of sodium and potassium. The slightly smaller values of the temperature coefficients suggest that the metals used in this work may not have been quite as pure as those Northrup used.

SUMMARY

- 1 The electrical conductivities of sodium, potassium, and sodium potassium alley have been measured and the results are in agreement with the values obtained by Northrup.
- 2 The heat conductivities of the alkali metals have been measured for the first time, as far as known.
- 3 The temperature coefficients of these conductivities have been determined.
- 4 The resistance-temperature coefficients of potassium and so-dium are extremely high.
- 5 The values of the ratio $\frac{C}{\lambda}$ for the alkali metals are extremely high.
- 6 The alkali metals behave in no exceptional way as regards the absolute values of the thermal and electrical conductivities at ordinary temperatures.
- 7 As a check on the method, the ratio % was determined for lead at room temperature and the value agrees with the one obtained by Jaeger and Diesselhorst.
 - 8 A modification of the electron theory of metallic conduction



has been suggested which accounts for the variation of the specific heat with the temperature, and also explains the curves which Le s obtained for the ratio $\frac{\lambda}{6\pi}$ for the pure metals at low temperatures.

In conclusion, I wish to acknowledge my indebtedness to Professor A. P. Carman who has followed this work with continued interest, placing at my disposal all the facilities necessary for the investigation; and to Professor Jakob Kunz, under whose direction the work was done, for many good suggestions and for invaluable assistance in filling the tubes. I also wish to thank Dr. G. McP. Smith of the Chemistry Department, who analyzed the metals used in this investigation.

Laboratory of Physics University of Illinois Nay 1913



BIOGRAPHICAL

John W. Hornbeck was born at Exeter, Illinois, May 21, 1881. He received his early education in the public schools of Pike County, Illinois, graduating from Perry High School in 1898. Ho was Principal of Schools at Summer Hill, Illinois, 1904-1905. He attended Illinois Wesleyan University four years and received the B.S. degree in 1906. For the next two years he taught mathematics in the Academy of Park College. He was scholar in physics at the University of Illinois 1900-1909; assistant in physics, University of Illinois, 1909-1910; assistant in physics, Cornell University, 1910-1911; instructor in physics, University of Illinois, 1911-1913. He received the degree of A. M. in physics at the University of Illinois in 1909. His graduate work was done during a period of four years at the University of Illinois and one year at Cornell University.





